

X-ray studies on the structure and Debye characteristic temperature of microcrystallites of graphitic carbon

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The radial distribution function, degree of graphitisation and the crystallite sizes for natural and artificial graphite samples have been determined from X-ray diffraction data. Effect of crystallite size on the radial distribution function as well as the Debye characteristic temperature of the samples has been studied.

1. INTRODUCTION

Many works on the structure of graphitic carbon have appeared in literature. Warren (1941), Warren & Bodenstein (1965, 1966) and others have studied both theoretically and experimentally the structure of graphitic carbon by postulating that it consists of parallel layer groups made up of individual graphite layers which are stacked roughly parallel to each other but random in orientation with respect to the axis normal to the layers. Mitra (1958) has studied the occurrence of periodic defects in the graphite like lattices due to the introduction of oxygen and hydrogen atoms in the lattice. Frankline (1950) has reported radial distribution analysis studies on graphite. As has been pointed out by Nicholas *et al* (1972), the particle sizes have considerable effect on the calculated radial distribution and since none of the previous works had taken this factor into account, a redetermination of the radial distribution function considering the particle size effects would be worthwhile.

Due to increased contribution of the surface atoms marked change in the Debye temperatures of micro crystals of various metals have been reported by several workers. As no such work has been reported for graphite, the Debye characteristic temperature has also been determined from the radial distribution functions.

2. EXPERIMENTAL

Measurement of diffracted intensities :

The radial distribution studies were carried out on two samples of natural and artificial graphite supplied by M/s. Graphite India Ltd, Durgapur. The natural and the artificial ones have been denoted as samples I and II respectively. Examination of the Debye Scherrer photographs of both the samples showed that the samples were free from preferred orientation. The photographs did not show

halos characteristic of the amorphous materials but rather showed diffuse lines indicating thereby that the samples have already acquired a high degree of graphitization. The samples were finely powdered and were passed through a sieve having 200 mesh per square inch. The finely powdered samples were placed in the rectangular slot of the sample holder and pressed till the slot was filled uniformly with the sample. Intensities were recorded with the help of Norelco wide angle X-ray diffractometer using CuK_α radiation. The intensities were recorded by point counting technique at intervals of 0.1° and the number of counts were so chosen as to keep the statistical fluctuations below 1%. Mean of the intensities recordings for several such runs was taken for the calculation of the radial distribution of intensities.

Calculation of the radial distribution function

The observed intensities were converted to absolute values in electron units by conventional methods (Klug & Alexander 1954). The radial distribution function (r.d.f.) was calculated using the relation

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho(0) + \frac{2r}{\pi} \int_{S_{\min}}^{S_{\max}} s i(s) (\exp(-bs^2)) \sin sr ds, \quad \dots (1)$$

where
$$i(s) = \frac{I(s) - f^2}{f^2}$$

$s = \frac{4\pi \sin \theta}{\lambda}$, λ is the X-ray wavelength, $I(s)$ is the coherently scattered intensity in electron units, f the atomic scattering factor and 2θ is the scattering angle. $\exp(-bs^2)$ is an artificial temperature factor introduced for minimising the series termination effects. $4\pi r^2 \rho(r)$ gives the mean number of atoms lying in a spherical shell between r and $r+dr$ and $\rho(0)$ is the atomic density.

The obtained r.d.f.'s were corrected for the effect of finite particle sizes following the method described by Nicholas *et al* (1972). The modified r.d.f. in case of a rectangular parallelepiped is given by

$$4\pi r^2 \rho'(r) = \frac{4\pi r^2 \rho(r) - 4\pi r^2 \rho(0) f'(r)}{f(r)} \quad \dots (2)$$

where
$$f(r) = 1 - \frac{r(ab+ac+bc)}{4abc} + \frac{r^2(a+b+c)}{16abc} - \frac{r^3}{64abc}$$

$$f'(r) = 1 - f(r)$$

and a, b, c are the dimensions of the crystallite.

In the present case the dimensions of crystallites parallel and perpendicular to the layers were calculated from the observed diffracted intensities following

the method described by Warren (1941). L_c , the size of the crystallites perpendicular to the layer was computed from (002) band and L_a the size of the crystallites parallel to the layers was calculated from (11) band. For modified i.d.f. the dimensions of the crystallites were taken as $c = L_c$ and $a = b = (2a)^2 = L_a^2 \sin 60^\circ$.

Determination of Debye characteristic temperature

The usual X-ray methods for determination of the Debye-Waller factor were not applicable in the present case because of the diffuse nature of the reflections and the changes in the intensities due to the large amount of faults present in the stacking of the layers like the stacking faults, variability of the interlayer separation etc. Hence the method by Morimoto (1958) was adopted in the present case. The radial distribution function, which is the Fourier transform of the measured intensity in the reciprocal space, directly gives the atomic arrangement and the half intensity width of the peak gives the r.m.s. amplitude of vibrations of the atoms. Kaplow (1972) has also discussed the utility of the r.d.f. for studying vibrations of the atoms both in the harmonic and anharmonic approximations. Mitra & Chaudhuri (1972) have applied the method for studying the Debye characteristic temperature of thin films of copper. As has been shown in Mitra & Chaudhuri (1972), the integral width 2β of the peak is related to r.m.s. amplitude of thermal vibrations and the damping factor b^2 by the relation,

$$\beta^2 = \frac{\bar{u}^2}{3} + b^2 \quad \dots (3)$$

$$\bar{u}^2 = \frac{h^2}{m_a k T} f(x), \quad \dots (4)$$

where h is Planck's constant, k , Boltzmann constant, T temperature in Kelvin, and m_a the mass of the atom;

$$f(x) = \frac{\phi(x)}{x^2} + \frac{1}{4x}$$

$$\phi(x) = \frac{1}{x} \int_0^x \frac{\xi d\xi}{e\xi - 1}$$

$$x = \frac{\Theta}{T}$$

and Θ is the Debye temperature factor. Thus $f(x)$ can be determined from the measured \bar{u}^2 and from the measured β^2 and from a plot of the theoretical curve $f(x)$ versus x , the value of x and Θ corresponding to a particular $f(x)$ can be calculated.

3. RESULTS AND DISCUSSION

The plots of the radial distribution function and modified radial distribution function for the two samples have been shown in figure 1 and figure 2 respectively. The values of the layer dimensions, the amount of unorganised

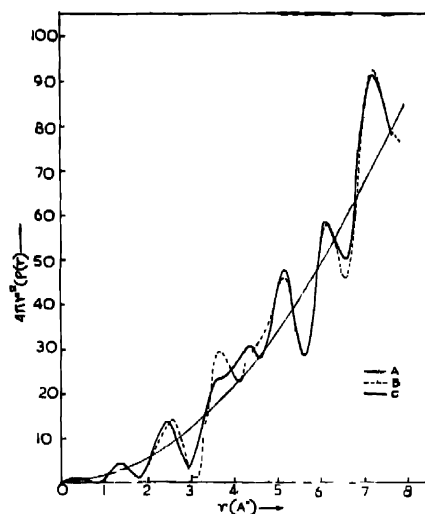


Fig. 1 Radial distribution function, $4\pi r^2 \rho(r)$, for sample I(A) and sample II(B) $4\pi r^2 \rho(0)$ shown as C

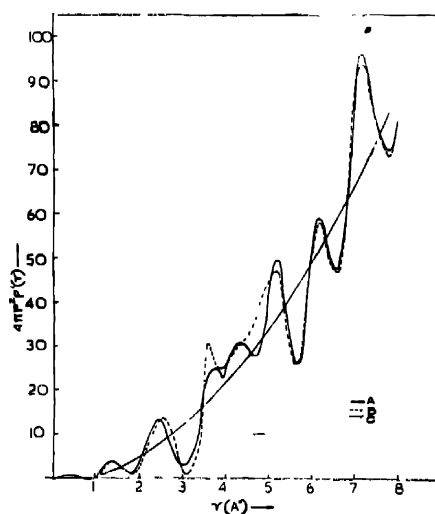


Fig. 2. Modified radial distribution function, $4\pi r^2 \rho'(r)$, for example I(A) and sample II(B). $4\pi r^2 \rho(0)$ shown as C.

carbon present and the Debye temperature of the samples have been given in table 1.

Table 1 : Crystallite sizes of samples

	Sample I	Sample II
Crystallite size II to layers (L_a)	40Å	195Å
Crystallite size I to layers (L_c)	59Å	63Å
Extent of amorphous carbon	20%	16%
Debye temperature Θ_D	200°K	215°K

Θ_D for bulk sample of graphite is 420°K Blatt (1968)

It was observed that the patterns obtained for both the samples showed broad lines indicating considerable graphitisation of the samples. The bands were markedly sharper in case of carbon II. The measured interlayer spacing value in the 002 direction for carbon I and II were 3.379Å and 3.361Å respectively. This suggests that carbon II has acquired greater degree of graphitization than carbon I.

The layer dimension in the directions perpendicular to the layer L_c were determined from (002) reflections and were found to be 55Å and 63Å for carbon I and II respectively. The values of L_a for carbon I and II were found to be 40Å and 195Å respectively.

It was observed from figure 2 that the differences in the r.d.f. of the two samples reduced, specially for higher r values, on applying the crystallite size correction.

The temperature factor $b = .01\text{Å}^2$ was found to be the optimum value as it considerably suppressed the near origin spurious peaks. The number of neighbour for the atoms were calculated from the area under the peaks. The r.d.f. curves indicate 2.7 nearest neighbours at a distance of about 1.40Å and 9.3 second nearest neighbours at a distance of about 2.50Å for carbon I. The curve for carbon II shows 3 nearest neighbour at 1.40Å and 9 second nearest neighbours at 2.6Å. All these positions are in agreement with the values for a single graphite layer.

Amount of non-organised carbon was calculated by fitting experimental and theoretical curves for the (11) band using the method of Franklin (1950, 1951). It was found that 20% and 16% of the carbon atoms did not participate in the formation of the parallel stacking of layers for carbon I and carbon II respectively.

The values of the Debye characteristic temperature as calculated from the radial distribution functions are 200°K and 215°K for carbon I and carbon II respectively. These values of Debye temperatures are much less than the bulk value of 420°K.

(Blatt 1968). Such large decrease has also been observed by other workers in case of small particles of materials—e.g., Petrov & Kotilnikov (1972) have reported the values of Debye temperatures of 234 Å. Au and 272 Å Cu particles to be 150°K and 276°K respectively which are much less than the bulk values of 185°K and 310°K. Such decrease has been explained to be due the larger ratio of the surface to bulk atoms, has larger r.m.s. displacements and hence smaller Debye temperature values. Further the occurrence of lattice defects changes the Debye temperature remarkably (Mitra & Chattopadhyay 1972). Therefore the observation that the Debye temperature of sample I is smaller than sample II and that both the values are much smaller than the bulk value can be attributed to the greater share of the surface atoms and the occurrence of lattice defects since the crystallite sizes of sample I is smaller than that of sample II.

4. CONCLUSION

From the radial distribution studies it was observed that there is greater graphitisation in sample II than sample I which was evident from the larger crystallite sizes and lesser amount of nonorganised carbon. It was also observed that with a decrease in crystallite size, there is considerable increase in values of the amplitude of thermal vibration of the atom, thus resulting in a decrease in Debye temperature values. Further work on the quantitative correlation of the amplitude of vibration of the atoms with the microcrystallite sizes is in progress.

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